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January 31, 2001

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the first quarterly report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc:	R. Sutula	DOE/OAAT
	K. Heitner	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	J. Krupa	DOE-Oakland

LBID-2353

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT

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BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to establish a test vehicle for the evaluation of new materials for high-power and low-cost Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. This task is a collaborative effort, which includes the development of an appropriate test vehicle (cell geometry), electrochemical cycling, and cell disassembly. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell with appropriate ratios of components (*i.e.*, active materials/electrolyte volume) and tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PI's involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, *i.e.*, Li metal/polymer/V₆O₁₃, will be carried out in the Electrolyte Task.

STATUS OCT. 1, 2000: This is a new project.

EXPECTED STATUS SEPT. 30, 2001: We expect to have semi-automated electrode preparation hardware in place. We expect to have pouch cell production hardware in place. We expect to have baseline evaluations of Swagelok cells (and button cells) carried out with baseline materials received from Quallion Corp. and a full testing protocol set up. We also expect to have a prototype web site set up with data from evaluation/testing of baseline cells from Doo Youn Corp. and Quallion Corp.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is the establishment of cell fabrication and testing protocols. While the test protocols are almost completed, orders for electrode fabrication equipment were delayed by the late receipt of capital equipment funding. We are adjusting the date for this milestone to June 2001.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

A first-generation test protocol was developed using Doo Youn cells received from Korea. These cells are 640 mAh rated capacity and were received at about 50% state-of-charge with maximum current of 1C and lifetime of greater than 60% capacity retention at 300 cycles.

Table 1. Generation 1 Cell Test Protocol

#	Test Name	Charge	Discharge
1	Theoretical Capacity	(C/2 discharge to V_{\min}) CCCV to V_{\max} & I_{\min}	C/25 discharge to V_{\min}
2	OCV vs. DOD	CCCV to V_{\max} & C_{rated}	C/2 to 10% C_{rated} , 1 hr OC hold x 10
3	Pulse Power Capability	CCCV to V_{\max} & C_{rated}	current pulses I_{\max} & I_{base} per procedure #3*
4	Constant-Current Cycling	CCCV to V_{\max} and C_{rated}	C/2 to V_{\min} , for 80 cycles
5	repeat steps 3 and 4 until capacity falls below 60% C_{rated} , discharge cell to V_{\min} , disassemble and deliver components to diagnosticians		

* USABC Electric Vehicle Battery Test Procedures Manual, rev. 2

Progress on the two major components of the cell fabrication part of the milestone, electrode manufacture and test cell design, has also been made. Site visits were made to Quallion Corp. in Los Angeles, Mine Safety Appliances (MSA) in Maryland, and ANL in Chicago. In addition, discussions were held with Hydro Quebec on two occasions.

A decision was made to pursue pouch cells as test vehicles for both Li-ion liquid and gel-electrolyte cells. In the case of the liquid-electrolyte cells, external compression will be applied. A few of the fixtures used by ANL will be prepared and used for comparison purposes from drawings received. MSA was open about their techniques for the assembly and testing of pouch cells. This vehicle lends itself to the preparation of cells of varying sizes and precise determination of electrolyte volumes. Following the discussions with MSA, work has begun on the preparation of electrode slurries to be used in an automated coater. Until the coater is received, slurries will be coated by hand using a knife-edge and evaluated for homogeneity, porosity and performance in a small-area test cell (Swagelok cell).

A purchase order for a bench-top coating unit with unwind, coating, drying and rewind modules has been placed with Alliance EC, Susquehanna, PA.

- Further plans to meet or exceed milestones

A preliminary web site has been deployed at <http://Battdata.lbl.gov/> for the posting of data generated in this task. The data will be contained in a database for ease of maintenance.

- Reason for changes from original milestones

The date of the original milestone was adjusted back several months to account for the date expected for the receipt of the coater. This delay is due in part to the late receipt of capital equipment funding and in part to the unexpected long lead time for the popular coater of 22 weeks, maximum.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization Using X-Ray Diffraction and Chemical Analysis

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes.

OBJECTIVES: Accelerate evaluation of electrode materials by structural characterization of active components as received (or synthesized), following cell disassembly, and *in situ* during cycling.

APPROACH: Analyze cycled electrodes taken from baseline BATT Program cells, seeking deleterious phase transformations in the bulk of the active material and accumulated inactive decomposition products.

STATUS OCT. 1, 2000: This is a new task.

EXPECTED STATUS SEPT. 30, 2001: Establish active material compositions of cycled and uncycled electrodes from Cell Development and Cathode investigators (Striebel and Doeff). Correlate phase transformations and accumulation of decomposition products with cell cycling performance.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

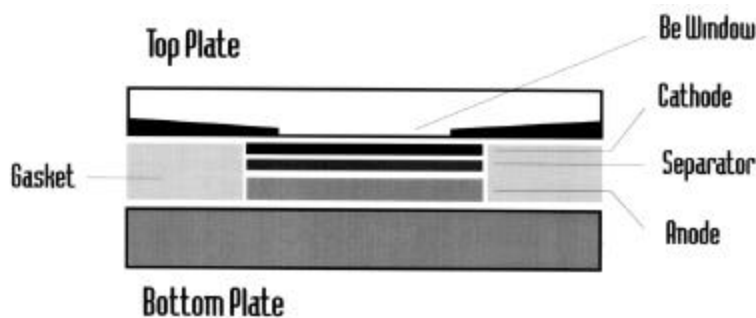
MILESTONES: Determine phase compositions in cycled electrode materials by the planned date of June 1, 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:** Although the start of this task has been delayed pending reclassification of the PI, design and fabrication of hardware for *in situ* x-ray diffraction have been completed. Baseline XRD patterns for commercial cells received from K. Striebel have been recorded and analyzed. Progress has been made toward hiring a post-doctoral fellow, who will also work with M. Doeff.

The goal of this task is to identify phase transitions and reaction by-products that contribute to capacity loss in the Li battery systems being investigated in the BATT program. The approach is to use x-ray diffraction (XRD) and spectroscopic techniques to analyze the solid components of composite electrodes at various stages of their cycle life, and to correlate changes in composition with cell deterioration and/or failure. In addition to data obtained from the cells provided by the Cell Development task, chemically and electrochemically treated active electrode materials are prepared and characterized to identify the phases that may possibly be present in cycled electrodes.

To date, sampling hardware for *in situ* XRD experiments (Fig. 1) has been designed and built. In the first stages, flat cells with beryllium windows will be studied in reflection mode. Once the capability to produce pouch cells at LBNL is realized, these will be examined in transmission geometry, which reduces the effects of x-ray attenuation due to absorption by containment materials.



Positive electrodes removed from a Doo Youn cell, which vented during short-term high-temperature cycling, were examined and found to have sustained no significant decomposition. Many more cells are still being cycled, and these will be analyzed after they have been dismantled.

Positive electrode active materials including LiFePO_4 and Li_xMnO_2 will be characterized prior to use in cell fabrication. Their oxidation and reduction products will also be prepared and characterized so that they can readily be identified in cycled electrodes.

- **Further plans to meet or exceed milestones:** It is anticipated that the milestone will be achieved on time.
- **Reason for changes from original milestones:** N/A

BATT TASK 2 ANODES

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Anodes - Carbon Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: High Cost of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify a low-cost carbon (<\$10/kg) for negative electrodes in Li-ion batteries for electric and hybrid vehicles.

APPROACH: We will continue our collaboration with industry (mainly HydroQuébec) to develop low-cost carbons for Li-ion batteries. Our role will be to utilize the analytical and spectroscopic facilities at LBNL to characterize the properties of the carbons. Techniques such as high-resolution electron microscopy, scanning electron microscopy, Raman spectroscopy, x-ray diffraction analysis and thermal analysis will be used to determine the physicochemical properties of carbon. Electrochemical studies to determine the reversible capacity and irreversible capacity loss of the carbons will be conducted in laboratory-scale cells.

STATUS OCT. 1, 2000: Our results suggest that there is a strong correlation between the irreversible capacity loss and the relative fraction of edge sites associated with the graphitized carbon sample. Within the range of graphite particle sizes considered in the study, there is no significant correlation between reversible capacity and the structural parameters associated with the crystallite size (*i.e.*, L_c , L_a). These results were obtained at reasonably low charge/discharge rates. We plan to examine these effects at higher rates to determine the influence of particle size on the initial reversible capacity. This study was conducted in collaboration with Hydro-Quebec.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical procedure that is lower cost than thermal purification processes to produce natural graphite for Li-ion batteries. The samples will be evaluated in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Develop low-cost carbon to meet the cost target for battery of <\$150/kWh.

MILESTONES: Complete analysis of particle-size effect on high-rate charge/discharge of flake graphite in liquid electrolyte. (03/01)

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

The intercalation rate of Li^+ -ions in flake natural graphite with particle size that ranged from 2 to 40 μm was investigated. The intercalation of Li^+ ions, and the reversible capacity, was determined at different C-rates following the definition by the battery community. For instance, the C/24-rate corresponds to 15.5 mA/g and C/4-rate is equivalent to 93 mA/g. The reversible capacity at these rates was determined from measurement of the coulombic charge corresponding to de-intercalation of Li^+ ions in 1 M LiClO_4 /1:1 (volume ratio) ethylene carbonate-dimethyl carbonate. The key issues in this study are the role of particle size and fraction of edge sites on the rate of intercalation and de-intercalation of Li^+ ions. At low specific current (15.5 mA/g carbon), the composition of lithiated graphite approaches the theoretical value, $x = 1$ in Li_xC_6 , except for the natural graphite with the largest particle size. However, x decreases with an increase in C-rate for all particle sizes. This trend suggests that slow solid-state diffusion of Li^+ ions limits the intercalation capacity of flake-like natural graphite. The flake natural graphite with a particle size of 12 μm may provide the optimum combination of reversible capacity ($x \geq 0.8$ at 93 mA/g) and irreversible capacity loss (35 mAh/g) in the electrolyte and discharge rates used in this study. Analysis of the area of edge sites and the intercalation current showed no dependence on particle size. This finding indicates that the transport of Li^+ ions in the electrolyte does not limit the intercalation capacity.

- **Further plans to meet or exceed milestones**

Milestone has been completed. Focus of this task will shift to development of low-cost graphite for Li-ion batteries. The effort will be conducted in collaboration with HydroQuébec.

- **Reason for changes from original milestones**

N/A

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and D. Curtis, University of Michigan

TASK TITLE – PROJECT: Anodes - Optimization of Anodes for Li-Ion Batteries

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety, irreversible capacity loss, and self-discharge.

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery, through development of a low-cost surface treatment process to stabilize the anode/electrolyte interface and reduce cell impedance.

APPROACH: Our approach is to coat the carbonaceous anode with an artificial SEI layer to provide superior thermal and chemical stability, as well as a high Li-ion conductivity for application in high-power Li-ion battery. The SEI will be engineered to be compatible with the other battery components and processes developed for ATD GEN II chemistry.

STATUS OCT. 1, 2000: We developed a Li-phosphonate based polymer stable in the operational voltage range of carbonaceous anodes with the added benefit of fire-retardant properties. We also developed a unique *in situ* technique to explore the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2001: We expect to fully incorporate the artificial SEI layer on a carbonaceous anode, and provide test results for improved rate capability, safety, and compatibility with using a lower cost and more stable electrolyte. The process developed in this research will also remove undesirable impurities and reactive surface groups from carbonaceous anodes. We expect also to provide a working mechanism and a model for the artificial SEI layer to guide the scale-up of this invention. This research work expects to provide a practical graphite anode for Li-ion technology.

RELEVANT USABC GOALS: Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries.

MILESTONES: Our milestones to synthesize and coat the anode with an artificial SEI, and provide performance test results are expected to be completed by the planned date, September 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have achieved high yield synthesis of a Li-phosphonate polymer to serve as an artificial SEI layer on graphitic anodes from low-cost chemicals. The electrochemical stability test of the polymer has been completed, and results indicate compatibility of the polymer with both anode and cathode of the Li-ion battery. The polymer was coated on microelectrodes, and tested for its chemical and electrochemical stability. Cyclic voltammetry results indicate chemical and electrochemical stability of the polymer in the working voltage range of fully lithiated graphite, LiC_6 . Further electrochemical tests show high Li-ion conductivity through this polymer film.

The Li-phosphonate polymer is also compatible with the mixed organocarbonate – LiPF_6 electrolyte. The stability of the polymer has been tested in the following mixed binary and ternary electrolytes: EC-DMC, EC-DEC, EC-EMC, and PC-EC-EMC containing 0.7M LiPF_6 .

- **Further plans to meet or exceed milestones**

Our immediate plan is to test the Li-phosphonate polymer in a small (2.54 cm diameter) Li-ion cell, and measure the interfacial impedance of the anode and the cell as a function of charge–discharge cycles. The rate capability of the electrode also will be tested from C/2 to 10C rates.

Thermal stability of the modified anode before and after charge–discharge cycles will be examined. The stability of the electrolyte during charge-discharge cycles will be studied using previously developed GC-MS and spectroscopy techniques.

- **Reason for changes from original milestones**

N/A

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-Cost Battery

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by x-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2000: We have identified intermetallic compounds with nickel-arsenide and zinc-blende structure types for possible exploitation as anodes for Li batteries. Cu_6Sn_5 and InSb were identified as test cases for the preliminary investigations of these types of materials, respectively; they yield reversible capacities of 200 mAh/g and >1000 mAh/ml for 10-15 cycles. These novel materials have exciting prospects for further development and improvement in performance.

EXPECTED STATUS SEPT. 30, 2001: Improvements in electrochemical performance from either new or modified intermetallic electrode compositions based on tin and antimony compounds will have been achieved. We expect to have improved the cycling stability of these materials with reversible capacities of 250 mAh/g and >1000 mAh/ml for 40 cycles. We will have obtained preliminary data regarding the thermal stability of the intermetallic electrodes with respect to organic-based electrolytes. We will also have gathered a more detailed understanding of the behavior of NiAs and zinc-blende electrodes in electrochemical cells.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: The primary milestone will be to increase the reversible electrochemical capacity of tin- and antimony-based electrodes from 200 to 250 mAh/g for 20 cycles by the end of April 2001, by which time preliminary calorimetric data will also have been gathered. A target of reaching a capacity of 250 mAh/g for 40 cycles by end of September 2001 has been set, by which time a greater insight of the electrochemical mechanisms of tin- and antimony-based systems will also have been gathered to enable the identification of cost-effective intermetallic electrode structures.

PROGRESS TOWARD MILESTONES

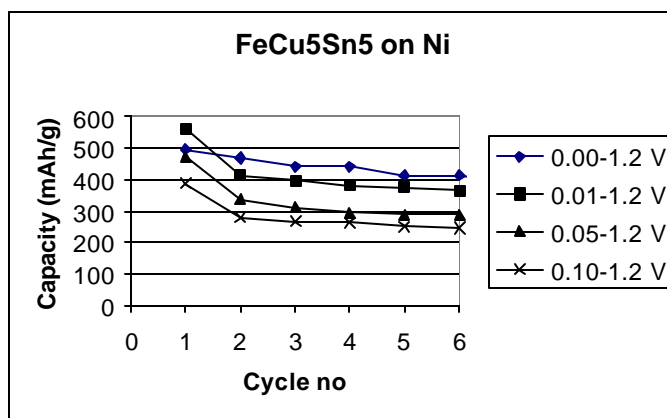
Accomplishments toward milestone over last quarter

Work over the past quarter has focused on Cu_6Sn_5 electrodes rather than InSb electrodes. Substituted $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ electrodes, where M is a transition metal, have been synthesized and evaluated in Li cells. In particular, we have concentrated our efforts on establishing the role of the current collector and of M substituents on the electrochemical performance of the system. It was observed that $\text{Li}/\text{Cu}_6\text{Sn}_5$ cells cycled to voltages below 200 mV appeared to operate by a different mechanism when the standard Cu current collector was replaced by Ni. *In situ* x-ray diffraction studies showed that with a Cu backing the reaction with Li at the working electrode is:



When a Ni current collector was used, the reverse-reaction to form Cu_6Sn_5 appeared to be impeded. The exact reason for the different electrochemical behavior is not known at this time although it is speculated that it may be related to some dissolution of Cu into the surface of the Ni current collector, or to a small amount of Ni incorporation into the host electrode structure that might suppress the phase transition from Li_2CuSn (cubic) to Cu_6Sn_5 (monoclinic).

Work has been initiated to study various substituted $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ electrodes in which M has been varied from Mn to Zn. For Fe-substituted electrodes (with Ni current collectors) a significant improvement in capacity retention has been obtained over the initial cycles compared with pure Cu_6Sn_5 electrodes. The figure below demonstrates how the capacity delivered by a FeCu_5Sn_5 electrode is significantly impacted by increasing the lower voltage limit of the $\text{Li}/\text{FeCu}_5\text{Sn}_5$ cells from 0 to 0.1 V; after 6 cycles between 1.2 and 0 V, the capacity is 410 mAh/g, whereas after the same number of cycles between 1.2 and 0.1 V, it is 240 mAh/g.



Further plans to meet or exceed milestones

Plans to collaborate with US industry are in place to accelerate the collection of calorimetric data (both isothermal and ARC) to determine the reactivity of the intermetallic electrodes with organic-based electrolytes.

Reason for changes from original milestones: N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-Cost Li-Ion Battery and Gel Battery.

BARRIER: Cost, safety and volumetric capacity limitations of lithium-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2000: We have determined that vanadium and manganese oxides, in their highest oxidation states, are probably not prime candidates. Pure aluminum was found to have a high capacity and to react readily with Li, but its capacity faded rapidly on cycling. Some simple binary alloys of aluminum and of tin have been identified and are being evaluated.

EXPECTED STATUS SEPT. 30, 2001: We expect to improve the electrochemical performance of the materials identified, to have completed a survey of all aluminum-based binary systems and their reactivity with Li, and to have identified several additional non-aluminum binary alloys. We will complete a study of the lower-valent MnV_2O_5 oxide.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify, by September 2001, a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li. In addition, we will identify all known aluminum binary alloys and their ability to react with Li by August 2001, and our assessment of MnV_2O_5 as an anode material will be completed by April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have investigated several binary Al compounds, such as aluminum carbide Al_4C_3 and aluminum boride AlB_2 , for their ability to react with Li. We hope by investigating such compounds that the large volumetric changes occurring during the reaction between pure aluminum and lithium can be ameliorated. These volume changes result in a rapid loss of capacity as shown in Fig. 1, although this appears to be strongly cell dependent.

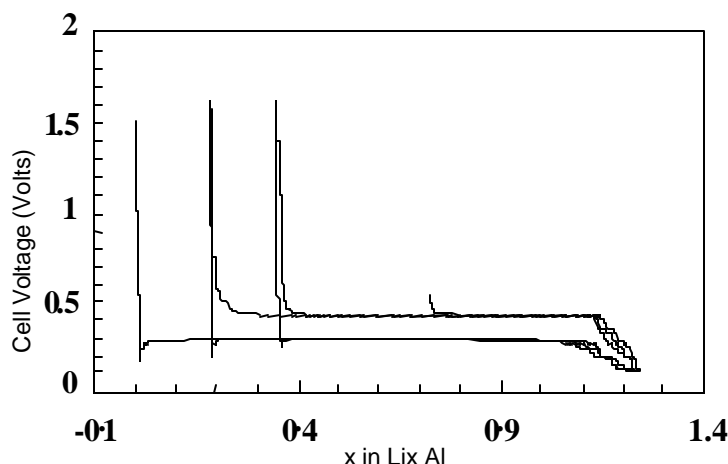


Figure 1. Cycling of aluminum metal in a clamped Swagelok cell.

The carbide reacts with 3 Li per formula unit on discharge between 0.8 and 0.05 V vs. pure Li, but less than 1 Li can be recovered on charge. The aluminum boride compound reacts with 0.8 Li per formula unit and up to half of this could be recovered on charging the cell. The initial capacity translates to 430 Ah/kg slightly higher than that of graphite, 340 Ah/kg. Little change in the x-ray diffraction pattern was observed after reaction.

French workers have made a study of MnV_2O_6 and have found positive results but with a low storage capacity; other French workers have noted higher levels of success using nano-sized oxide materials. MnV_2O_5 , a material first synthesized by us, should have a higher storage capacity because of its lower oxygen content. We have synthesized a sample for evaluation as an oxide anode, and expect to complete this study in the next quarter.

We are expecting delivery of a button cell set-up this month, which will allow for more reproducible cell systems.

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

Presentation

“Aluminum based anode materials for rechargeable batteries,” S. Yang, P.Y. Zavalij and M.S. Whittingham at the Materials Research Society National Meeting, Boston, December 2000. (to be published in meeting proceedings).

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Short lithium battery lifetimes, poor ambient temperature performance for polymer electrolytes and low energy and power densities as a result of polymer instability to 4-V cathodes.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (4 V) and develop materials and methods to increase stability.

APPROACH: Through a balance of synthesis, analysis, and modeling, a physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but the problem can be corrected through the materials design and synthesis capabilities thereby developed.

STATUS OCT. 1, 2000: Polymer synthesis capability has been established that facilitates the production of linear and branched polymer networks for use in Li/polymer batteries and polymer gel Li-ion systems. New polymers with significantly higher conductivities are now available as are polymer systems with higher voltage stabilities than PEO.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete a study of the effects of mechanical, chemical, and transport properties of polymer electrolytes on dendrite growth at Li metal electrodes that will provide data to allow the system to be accurately modeled. We expect to prepare and test polymer electrolytes with room-temperature performance and to define the upper limits of ion transport for polymer electrolytes. We expect to determine the practical cathode stabilities of polymer electrolytes with adequate transport properties.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONES:

1. Determine electrolyte properties that inhibit dendrite growth (September 30, 2001).
2. Determine the limits of Li ion mobility in polymer electrolytes (September 30, 2001).
3. Prepare bulk materials (100g) for testing in the BATT Li polymer (April 15, 2001) and low-cost Li-ion test systems (June 30, 2001).

PROGRESS TOWARD MILESTONES

1. Accomplishments toward milestone 1 over last quarter: Electrolyte properties of importance for the study of dendrite growth are transport properties, mechanical properties, and chemical reactivity. To measure transport and mechanical properties accurately, accurate measurement of the electrolyte dimensions is necessary. To this end a device for measurement of the electrolyte thickness has been built that should provide the necessary accuracy. Rheological equipment has been repaired and upgraded to allow routine measurement of mechanical properties of electrolytes. Several batches (>20g each) of comb-branch and linear cross-linkable polymers have been prepared, purified and characterized by GPC.

- **Further plans to meet or exceed milestones:** Include the preparation, characterization, and testing of cross-linked polymer membranes to determine how transport properties, mechanical properties, and chemical reactivity promote or inhibit dendrite growth. This task will provide data for the modeling group.
- **Reason for changes from original milestone:** N/A

2. Accomplishments toward milestone 2 over last quarter: Lithium-ion mobility in polymer electrolytes is governed by the solvation of the Li ion, ion pairing to the anions, and the polymer architecture. Further conductivity measurements on new polymers with solvating groups other than ethylene oxide have been carried out. More material has been synthesized to allow further testing of macrocyclic groups, linear comb-branch, and linear polymers. The synthetic method is less than optimal and efforts have been made to find better syntheses.

- **Further plans to meet or exceed milestones:** Collaboration with modeling groups in the BATT program and in the Office of Science program indicates that the approach will result in room-temperature polymer electrolytes. Synthesis and testing of these materials will be carried out in due course. Calculations carried out by Larry Curtis (ANL) indicate that higher conductivities than previously expected may yet be achieved.
- **Reason for changes from original milestone:** Plans for this milestone have fallen behind schedule due to unexpected reactivity of the polymers that leads to cross-linking. This problem is under study.

3. Accomplishments toward milestone 3 over last quarter: Large amounts (>100gm) of polymers are under preparation for testing in the BATT Li/polymer system and the low-cost polymer gel system. Comb-branch and linear cross-linkable materials have been prepared. Samples of PEO have been obtained from manufacturers and arrangements made with battery companies to facilitate the preparation of the polymer systems in practical and credible battery test systems.

- **Further plans to meet or exceed milestones:** Polymers electrolytes will be formulated with salts and electrode components to provide separators and composite electrodes. Appropriate transport and mechanical characterization will be carried out in addition to electrochemical cell testing. Scale up to 100cm² area is planned.
- **Reason for changes from original milestone:** Unexpected cross-linking of polymers has impeded progress. This may be due to poor control over molecular weight in addition to photochemical and thermal reactions of the ether units. This problem is under study in collaboration with polymer manufacturers.

TASK STATUS REPORT

PI, INSTITUTION: M. Ratner, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Modeling of Lithium/Polymer-Electrolyte Batteries

SYSTEMS: Lithium/Polymer, Gel Electrolyte

BARRIER: Reduced power density in lithium batteries.

OBJECTIVES: Our primary objective is the achievement of modeling-based design protocols for polymer electrolytes and polymer gel electrolytes, in lithium metal batteries.

APPROACH: This purely theoretical work uses both ab-initio electronic structure calculations to optimize anionic components of the battery electrolyte, and dynamic Monte Carlo calculations to understand and model the effects of polymer physical properties (including gelation and charge density) on the ionic conductivity, and therefore the power density, of electrolyte batteries.

STATUS OCTOBER 2, 2000: We had completed the electronic structure work, suggesting modalities for optimized anionic centers (delocalized charge, chemically “soft” centers, aluminosilicate rather than aluminate). Monte Carlo applications on the optimization of the phase diagram are beginning.

EXPECTED STATUS SEPTEMBER 30, 2001: We should have completed the phase diagrams for the comb/tooth polyelectrolyte (single-charge conductor) Li battery electrolyte. We will also have begun generalized dynamic percolation models for optimization of the gel component in gel electrolyte batteries, and analyzed the possible percolation pathways for such structures.

RELEVANT USABC GOALS: 10-year life, conductivity of 10^{-3} S/cm for stable electrolytes, 10^{-4} S/cm for single-charge conductors.

MILESTONES: We have completed the milestone on electronic structure modeling. The current challenging milestone is, by June of 2001, to have completed the phase diagrams for the percentage of charge density (Li bearing) vs. neutral (polyether) side chains on the soft backbone of designed polymer batteries.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have completed the milestone on electronic structure modeling. The current challenging milestone is, by June of 2001, to have completed the phase diagrams for the percentage of charge density (lithium bearing) vs. neutral (polyether) side chains on the soft backbone of designed polymer batteries. More specifically, Jim Snyder (a joint graduate student with Shriver) is calculating the conductivity as a function of the mole fraction of lithium containing side chain “teeth” on a soft hydrocarbon backbone. These comb/tooth motif structures are the most general context for charge Li conductors based on polymers.

- **Further plans to meet or exceed milestones:**

By June of 2001, we should have complete results for the homogeneous case. The milestone for the remainder of 2001 will involve the gel electrolytes.

- **Reason for changes from original milestones:**

We had proposed a static/dynamic percolation picture for optimizing the percentage of gel agent. Work on this will not begin until the phase diagrams are completed: we anticipate completing this part by January 2002.

Publications

Y-C. Lee, L.A. Curtiss, M.A. Ratner, D.F. Shriver, “Computational Studies of Lithium Affinities for Zeolitic Fragments,” *Chem. Phys. Letters*, **321** 463-468 (2000).

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M.A. Ratner, “Ionic Charge Transport in Molecular Materials: Polymer Electrolytes,” in D.A. Jelski, T.F. George, eds., *Computational Studies of New Materials*, 174-209 (1999).

G.S. Kedziora, J.A. Pople, V.A. Rassolov, M.A. Ratner, “The Relativistic Dirac-Coulomb-Fock Effect on Atomization Energies,” *J. Chem. Phys.* **110**, 7123-7126 (1999).

A.P. Alivisatos, P.F. Barbara, A.W. Castleman, J. Chang, D.A. Dixon, M.L. Klein, G.L. McLendon, J.S. Miller, M.A. Ratner, P.J. Rossky, S.I. Stupp, M.E. Thompson, “From Molecules to Materials: Current Trends and Future Directions,” *Adv. Mater.* **10**, 1297-1336 (1998).

M. Ratner, “Mathematics, Computational Chemistry, and Battery Building: Some Notions,” in *Modeling and Computation for Applications in Mathematics, Science, and Engineering*, J.W. Jerome, ed., 1-24 (1998).

J. Kolafa, M. Ratner, “Oligomers of Poly(Ethylene Oxide): Molecular Dynamics with a Polarizable Force Field,” *Molecular Simulation*, **21**, 1-26 (1998).

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/Polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2000: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C; have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^6 Pa); and, the presence of fumed silica enhances Li-electrolyte interfacial stability, although the extent and mechanism remain to be determined.

EXPECTED STATUS SEPT. 30, 2001: We expect to determine how fumed silica (hydrophobic R805 and hydrophilic A200) affect full-cell cycling using vanadium-based, 3-V cathodes and baseline PEO-type materials in coin cells. We also expect to identify to what extent fumed silica enhances interfacial stability in low-molecular-weight PEOs and begin extending the analysis to base-line PEO materials. We expect to characterize how interfacial stability is related to the mechanical properties, working in close collaboration with Kerr.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones to determine the effects of fumed silica (hydrophobic R805 and hydrophilic A200) on full-cell cycling and interfacial stability are expected to be completed by September 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have been in a transition period in the last quarter and are now focusing on the baseline system. In this regard, we have carried out full-cell cycling using manganese oxide cathodes, but will focus on vanadium oxide cathodes in the next quarter to comply with BATT guidelines. A post-doctoral candidate accepted our offer to work on the project but subsequently rescinded his acceptance due to personal reasons.

We have initiated our research on full-cell cycling using vanadium-based, 3-V cathodes. V_6O_{13} from Kerr-McGee, graphite SFG 15 from Timcal, and PVDF binder from Kynar are used as our cathode materials. We have been working on establishing a standard procedure and optimizing compositions of vanadium oxide cathodes. Full-cell cycling at 0.1 mA/cm^2 using vanadium oxide cathodes has also started with liquid electrolyte and 10% R805 composite.

The mechanism of ion transport and how to tune the electrolyte remains an area rich in opportunity and poor in consensus amongst researchers. We continued our study of the fundamentals of ion transport using techniques in NMR, rheology, and electrochemistry. Our research agrees with the overall view that the more motion a polymer chain has the better the total charge transport. However, at extremely high concentrations (those corresponding to Li:O:1:5) the charge transport is not optimum but the Li transference approaches 0.5 due to a restriction of the mobility of the anions. The lower conductivity may be acceptable under certain conditions given the higher Li transference number.

We have finished installing a computer-controlled impedance measurement system that can measure the impedance of up to ten samples as a function of temperature. The automated system was created in Bridgeview and interfaces with a serial-controlled programmable water bath and an EG&G PAR 273 potentiostat through EG&G's PowerSine software. The new system will significantly reduce the number of man-hours needed to measure conductivity.

- **Further plans to meet or exceed milestones**

We plan to hire a post-doc within the next quarter and continue full-cell cycling using vanadium-based, 3-V cathodes. Because the low-MW PEO is an analog for the high-MW system, we will initiate our efforts with this polymer. We will also focus on interfacial stability studies using base-line materials with fumed silica. In conjunction with Kerr, we will also focus on correlating mechanical properties to interfacial stability.

- **Reason for changes from original milestones**

Our milestones have been modified from the AOP submitted in July based on the reviewers' comments and after discussions with LBNL personnel (*e.g.*, Kerr) to be compliant with BATT guidelines and to make a synergistic tie with the electrolyte effort of Kerr's group.

TASK STATUS REPORT

PI, INSTITUTION: D.F. Shriver, S. Vaynman, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

SYSTEMS: Li/Polymer

BARRIER: Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

OBJECTIVES: The primary objective is to synthesize and test a new class of highly ionic-conductive, rigid polymer electrolytes for rechargeable Li batteries.

APPROACH: Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward the Li electrode. If this or related instabilities with sulfone-containing polymer electrolytes are encountered, we will prepare new polymer electrolytes. One such possibility is a bilayer electrolyte with an oxidation-resistant fluorocarbon backbone on one side and a reduction-resistant hydrocarbon or hydrocarbon ether backbone on the surface in contact with the Li electrode. At least two polymer-salt complexes and polyelectrolytes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li cells. Before polymers are synthesized we will test the stability of the small-molecule analogs of the polymers in contact with Li metal.

STATUS OCT. 1, 2000: We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity ($\sim 10^{-4}$ S/cm at room temperature), but are unstable toward Li. The ionic conductivity of a recently synthesized polymer-salt complex that contains sulfone functional groups is lower ($\sim 5 \times 10^{-6}$ S/cm at room temperature), but the stability toward Li is much higher than that of polymer-salt complexes that contain carboxy groups.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize and test in cells a number of sulfone-containing rigid polymer electrolytes and polyelectrolytes that display favorable ionic conductivity and good electrochemical stability toward battery components. Also, we expect to scale up the synthesis of the most promising electrolyte(s) and send them to LBNL for large-scale testing.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are:

1. To synthesize and test promising polymer systems by 6/2001 with the goal of conductivity higher than 10^{-4} S/cm at room temperature. The resistivity of the Li/polymer electrolyte cell should not increase more than twice during the first week of testing.
2. To scale-up the synthesis of the most promising polymer electrolyte and to send it by 10/2001 to LBNL for cell fabrication and testing.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter**

Our project focuses on:

- a. chemical synthesis of highly-ion-conductive rigid polymer electrolytes,
- b. study of the ion-transport properties of these electrolytes,
- c. investigation of interactions at the Li electrode/polymer electrolyte interface,
- d. testing of the electrolyte in a battery configuration.

During the last quarter we studied the stability of the polyarylsulfone (Fig. 1a) toward a Li electrode and tested this polymer electrolyte in a battery. These studies indicated that the polyarylsulfone-containing polymer electrolyte is much more stable toward Li metal than PVICOX, the rigid polymer-salt complex that contains carboxy groups. This polyarylsulfone-containing polymer electrolyte was tested in a Li/polymer electrolyte/ Li_xMnO_2 cell and a capacity of up to 100 mAh per gram of active cathode material was achieved at current density of $15 \mu\text{A}/\text{cm}^2$. However, the capacity was reduced significantly with an increase in current density to $40 \mu\text{A}/\text{cm}^2$ due to comparatively low conductivity of the polyarylsulfone-containing polymer electrolyte ($\sim 5 \times 10^{-6} \text{ S}/\text{cm}$ at room temperature).

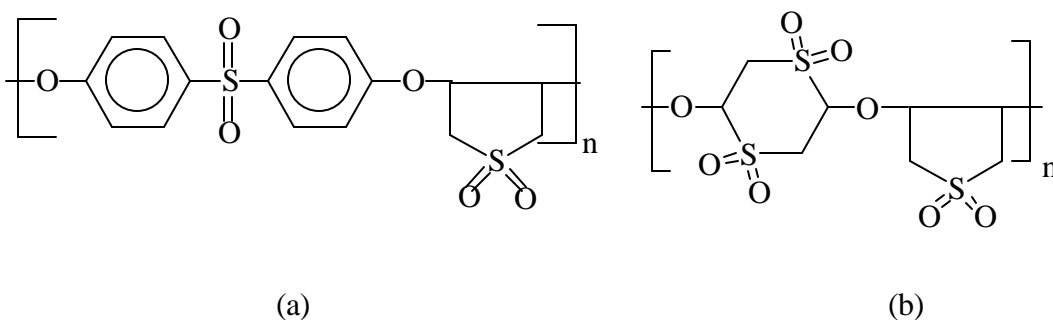


Figure 1. Structure of polysulfones under investigation.

Another sulfone-containing polymer (Fig. 1b) is being synthesized in our laboratory at the present time. We will explore different synthetic routes to this polymer with emphasis on high yield. We anticipate that when doped with salt, this polymer (b) will display higher ionic conductivity than that of polymer (a), because the polymer (b) has higher density of cation coordinating sites than (a). We also expect high stability of polymer (b) toward Li.

- **Further plans to meet or exceed milestones**

We expect to meet our milestone by synthesizing the sulfone-containing polymer (b) in the next month and then testing its stability toward Li. This will be followed by the testing of polysulfone/salt complex in a Li/polymer electrolyte/ Li_xMnO_2 cell.

- **Reason for changes from original milestones**

N/A

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: A study will be undertaken to identify suitable additives that function as a radical trap for the radical anions produced by solvent reduction. We propose to use this concept to identify species that are incorporated in the SEI layer to improve its stability. This type of reaction product will be evaluated as additives in gel and liquid electrolytes. Based on our studies of reaction products obtained by thermal decomposition of the electrolyte, compounds that decompose to form polyether and polycarbonate oligomers will be studied as additives. Electrochemical evaluation of additives to determine the reversible and irreversible capacity loss will be conducted in coin cells using the baseline liquid or gel electrolytes. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss of carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing a SEI layer.

STATUS OCT. 1, 2000: Experiments were initiated to determine the thermal stability of a baseline electrolyte [1 M LiPF₆ in a mixture of 1:1 EC/DMC]. The electrolyte was heated to 85°C, and samples were removed periodically for analysis by gas chromatography (GC). The GC trace from the electrolyte mixture shows two clearly separate solvent peaks for DMC (5-min retention time) and EC (about 14.1-min retention time) as well as a large new peak at 13.8-min retention time and several others of lower intensity. The peak intensity for EC decreases as a function of storage time, indicative of the gradual decomposition of EC at 85°C. On the other hand, the GC signal for DMC remains essentially constant in intensity, indicating that DMC is stable during storage at 85°C. The major new compound was identified as diethyl 2,5 dioxahexane carboxylate (DEDOHC), which increases with time of storage at 85°C.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical additive that enhances the thermal stability of the SEI layer on carbon. The additives will be evaluated in a liquid electrolyte to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES:

1. Identify desired structural features of additives that enhance SEI properties (12/00).
2. Evaluate the effect of polycarbonates as additives for improving the thermal stability of the SEI layer on carbon electrodes (9/01).

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone 1 over last quarter

A survey of recent US patents and research publications was undertaken to identify the desired structural features of additives that enhance SEI properties at negative electrodes in Li-ion batteries. Electrolyte additives serve many functions in Li-ion batteries, such as

- Improve electrolyte nonflammability
- Improve stability of SEI layer
- Minimize gas evolution in cell
- Decrease first-cycle capacity loss
- Enhance cycle and calendar life

Overcharge protection involving a redox shuttle or monomer additive that polymerizes at voltages greater than maximum operating voltage

The evidence suggests that additives and/or degradation products of the additives should be incorporated in the SEI layer to enhance its stability. Acceptable additives should have the following characteristics:

1. soluble in the electrolyte
2. can be modified to a reduced state substantially without forming a gas
3. form a passivating layer to substantially block the electrolyte solvent from contacting the carbonaceous surface to prevent gas generation
4. increase first-cycle coulombic efficiency
5. reduce capacity fade.

- Further plans to meet or exceed milestone

Experiments will be conducted with additives that are expected to decompose during the initial intercalation (charge) of carbon electrodes in the baseline electrolyte. Samples of ATD GEN 1 anodes that were lithiated in baseline electrolyte, with and without additives [polycarbonate from LBNL and IIT flame retardant (hexamethoxy-tri-aza-phosphazene)] were received. TEM analyses will be conducted to determine if the SEI layer can be observed and if the additive has an affect on the structure of the SEI layer.

- Reason for changes from original milestone: N/A

- Accomplishments toward milestone 2 over last quarter

Based on our analysis, additives and electrolyte solvents that form intermediate radical anions during cathodic reduction (*i.e.*, during the formation step in Li-ion batteries) are desirable to produce a stable SEI layer. Reactions of the intermediate radical anions with the solvent and/or the additive, before further reaction of the solvent to form gaseous species, are expected to form more stable SEI layers. Polymerization of the degradation products may also be involved to enhance the stability of the SEI layer.

- Further plans to meet or exceed milestone

We are in the process of hiring a post-doc to conduct the research.

- Reason for changes from original milestone: N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point ($>100^{\circ}\text{C}$), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V vs. Li); and (2) to evaluate anode and cathode (being developed in the BATT Program) materials in coin cells using thermal diagnostic methods.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the baseline Li-polymer and low-cost Li-ion cells using differential scanning calorimetry (DSC), isothermal microcalorimetry (IMC), and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2000: We completed the synthesis of the flame retardant (FR) hexa-methoxy-tri-aza-phosphazene $\text{N}_3\text{P}_3 [\text{OCH}_3]_6$ and supplied 10 gram of this material to the ATD Program (ANL and PolyStor) for further testing in PNGV Li-ion cells. We also completed the thermal and electrochemical characterization of this FR additive in Li-ion cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize two flame-retardant additives, hexa-ethoxy-tri-aza-phosphazene (HETAP) and urea-diphosphonate (URDP), and characterize their electrochemical and thermal behavior in low-cost Li-ion cells. We also expect to complete the synthesis and characterization of two thermally stable and corrosion-resistant modified imide salts $\text{LiN}(\text{SO}_2\text{X})_2$ ($\text{X} = -\text{CF}(\text{CF}_3)_2$ and $-\text{C}(\text{CF}_3)_3$). In addition, we expect to characterize the thermal behavior of Li-ion cells containing graphite and Sn-based anodes, $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode in $\text{LiPF}_6\text{-EC-EMC}$ and LiBF_4 + cross-linked gel electrolyte.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES:

1. The scale-up synthesis of the FR additive HMTAP and the thermal characterization of the FR additive HETAP are expected to be completed by the planned date of April 2001.
2. The thermal characterization of graphite anode (for comparison purposes) using IMC and DSC is also expected to be completed by April 2001.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone 1 over last quarter

- 1) During the last quarter, we completed the synthesis of the flame retardant (FR) hexa-methoxy-tri-aza-phosphazene $N_3P_3[OCH_3]_6$ (HMTAP) and supplied 10 gram of this material to the ATD group (Argonne National Laboratory) for further evaluation in PNGV Li-ion cells.

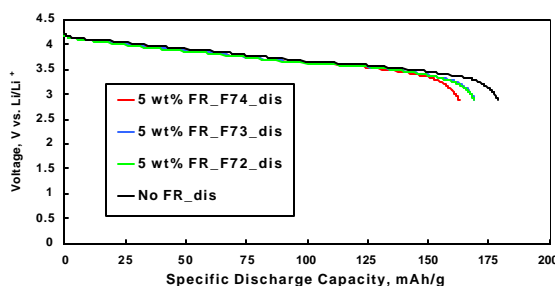


Figure 1. Effect of the electrolyte with various wt% HMTAP on the performance of Li-ion cells.

- 2) We completed the thermal and electrochemical characterization of this FR additive in cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC, and investigated the effect of amount of the HMTAP on the performance of the Li-ion cells. Various amounts of the FR additive HMTAP (1 to 10 w%) were used in these Li-ion cells. The results of these studies are shown in Fig. 1. It can be seen from this figure that there is no detrimental effect of the amount of the FR additive on the Li-ion cell performance.
- 3) We also presented a paper entitled “Studies on electrochemical and thermal properties of Li-ion battery electrolytes with different salts” at the Phoenix ECS Meeting (Abst. 143)

- Further plans to meet or exceed milestones

We plan to complete the scale-up synthesis of the FR additive HMTAP and provide the sample to ANL in order to reproduce the previous results obtained by ANL on Li-ion cells. In addition, we also plan to collaborate with LBNL in carrying out investigations dealing with the HMTAP in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte at higher temperatures.

We will also develop new flame retardant additives [hexa-ethoxy-tri-aza-phosphazene and urea-diphosphonate) and new Li-salts with high conductivity and high thermal stability to reduce self-heat rate (SHR) especially at higher temperatures during thermal runaway.

- Reason for changes from original milestones

The evaluation of the HMTAP carried out in collaboration with ANL showed that the presence of FR additive increases the onset of the thermal runaway of the Li-ion cells by more than 25°C. This shift is very encouraging for the safety of the Li-ion cells. However, the SHR at temperatures beyond 265°C was found to increase in presence of HMTAP. In order to address the issue of SHR at higher temperatures and to meet the milestone, we will also pursue new FR additives as described in section B with reduced SHR at higher temperatures as a possible replacement for HMTAP.

TASK STATUS REPORT

PI, INSTITUTION: A. McEwen, Covalent Associates, Inc.

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes for Li-ion Batteries

SYSTEMS: High-performance nonflammable electrolytes for Li-ion batteries

BARRIER: Limited thermal stability of Li-ion electrolytes

OBJECTIVES: The primary objective is to develop nonflammable electrolytes for Li-ion batteries to meet DOE safety goals. These electrolytes will be optimized for the cell objectives for liquid electrolytes outlined by the BATT program.

APPROACH: Our approach is to synthesize new ionic liquids and to formulate these into Li-ion electrolytes with the addition of Li salts and common solvents. We determine their suitability by measuring conductivity, Li intercalation, and cycle life of half-cell and full-cell batteries using these new electrolytes. Flammability and flashpoint of the electrolytes are determined.

STATUS OCT. 1, 2000: We demonstrated a long-lived Li-ion battery using a nonflammable ionic-liquid-based electrolyte. Over 40 cycles were obtained from a graphite/LiCoO₂ coin cell battery.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify an optimum nonflammable ionic liquid formulation for Li-ion battery electrolytes based on performance and price. The compatibility of these ionic liquid electrolytes will be determined with the systems of interest. We will investigate alternative cathodes and anodes from the LiCoO₂ cathode and lithium and graphite anode we are working presently with in our feasibility studies. Specifically, the LiFePO₄ and Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.92}S_{0.03} positive electrode and Sn-based negative electrode will be assessed with our novel nonflammable electrolytes. We will also assess the performance of the inexpensive lithium salt LiTFSI in the ionic liquid formulations.

RELEVANT USABC GOALS: High-performance nonflammable electrolytes/low-cost electrolytes.

MILESTONES: Our major milestone to demonstrate a nonflammable Li-ion electrolyte based on ionic-liquid technology should be completed by the planned date of April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Using a nonflammable electrolyte, formulated with an ionic liquid, carbonate solvent, and 1M LiPF₆ salt, we obtain good cycling behavior (Fig. 1) in coin cells using graphite cathodes and LiCoO₂ anodes. These imidazolium based ionic liquids form stable SEIs on graphite with the small addition of carbonate solvents. Although carbonate solvents are flammable, in these ionic liquid formulations there is no flash point or burning in the flammability tests.

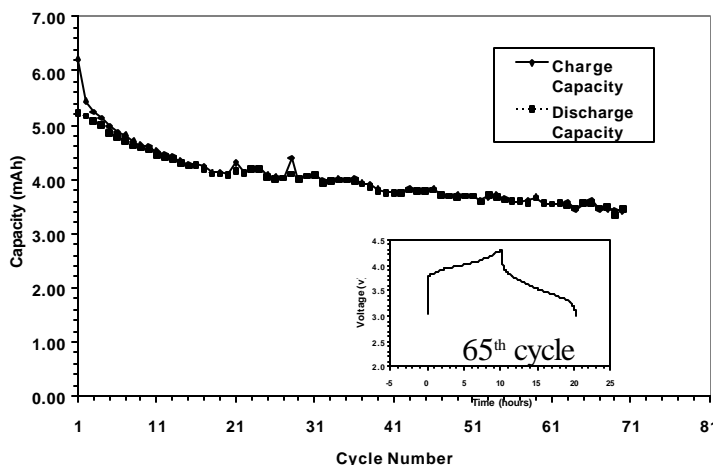


Figure 1. Capacity as a function of cycling for a graphite/LiCoO₂ coin cell.

- **Further plans to meet or exceed milestones**

We have demonstrated the use of ionic liquid based electrolytes for Li-ion battery systems. We plan to optimize the discharge rate capability, cycle life, and minimize the cost of these new nonflammable electrolytes.

- **Reason for changes from original milestones**

After the failure of the fluorinated esters to meet the nonflammable criteria, we initiated an investigation into using Covalent's proprietary Ionic Liquids (US Patent 5,827,602) as Li-ion electrolytes. We shifted the focus of the project to investigate these novel materials that have a wide liquid range, high thermal stability, and lack a vapor pressure. In addition, they are nonflammable and non-corrosive, giving them a thermal application range from below room temperature to approaching 400°C. Initial results using Covalent's ionic liquid based electrolytes for Li-ion batteries were very promising. We demonstrated the reversible intercalation into graphite using an ionic liquid formulated electrolyte and obtained good results with a lithium metal/LiCoO₂ cell. We are also obtaining very promising cycling results using an ionic liquid based electrolyte in a Li-ion battery using graphite and LiCoO₂ electrodes at 4.3 V.

TASK STATUS REPORT

PI, INSTITUTION: K. Wheeler, Delaware State University

TASK TITLE - PROJECT: Electrolytes - Development of Novel Sulfone Based Electrolytes for Rechargeable Lithium Battery Applications

SYSTEMS: Li/Polymer

BARRIER: Electrochemical Stability

OBJECTIVES: The primary objectives are to fabricate and determine the structure-electrochemical stability properties of a series of sulfone cross-linked PEO polymers.

APPROACH: Our approach is to utilize standard organic preparative methods to synthesize a homologous series of sulfone cross-linked PEO polymers. Synthetic strategies include condensation of PEG's with 3-chloro-2-chloromethyl-1-propene with alkali conditions to produce the expected co-block 1D polyethers. Further reaction of the polycondensate will follow a radical initiated cross-linking with divinylsulfone to give the expected sulfone cross-linked PEO polymers. Additional studies include determination of the structural features and the electrochemical stabilities of these polymer electrolytes with cells that use platinum microdisc (working) and lithium strip (reference and counter) electrodes.

STATUS OCT. 1, 2000: We have prepared and characterized three sulfone cross-linked PEO polymers based on 400, 2000, and 4600 MW PEG precursors and defined relationships between electrolyte composition and electrochemical stability.

EXPECTED STATUS SEPT. 30, 2001: We expect to characterize the electrochemical susceptibility of polymeric sulfone cross-linked PEO/LiIm electrolytes under varying conditions and to identify key pathways of degradation of these electrolytic systems. We expect to determine the role of the sulfone functionality as related to electrolyte performance.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: The major milestone of the program centers on improving preparative methods and determining the influence of key chemical features of the sulfone and polymeric units to the electrochemical processes. Milestone is expected to be achieved by April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Improvements with synthetic methodology show increased reaction yields and material purities for the three sulfone cross-linked PEO polymers based on 400, 2000, and 4600 MW PEG precursors.

Voltammetric experiments performed at 25°C with the polycondensates swelled in 0.1 M LiIm CH₃CN solutions reveal the onset of polymer decomposition at ~4.0 V *vs.* Li. Subsequent preparation and analysis of additional samples of the polyelectrolytic materials confirmed the reproducible nature of the observed electrochemical processes.

- **Further plans to meet or exceed milestones**

Exploit key structural features of the current polycondensate electrolytes for the rational design and synthesis of new electrolytic materials with improved cell performance.

Elucidate the chemical details of polymer electrolyte decomposition.

Determine the correlation between polymer chain length and composition to electrochemical performance.

- **Reason for changes from original milestones:** NA

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-Cost (Li-Ion) Battery and Li-Polymer Battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt/nickel electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel on electrochemical cycling, particularly those derived from Li_2MnO_3 ; for Li-polymer cells, the material of choice is stabilized $\alpha\text{-MnO}_2$. (Note: At this stage of the project, we have downgraded the research priority to search for an alternative vanadium oxide electrode, such as V_6O_{13} , to replace the current material of choice, LiV_3O_8 , because in the Li-V-O system, LiV_3O_8 is still believed to be the best vanadium oxide electrode available for Li-polymer cells.)

STATUS OCT. 1, 2000: We have exploited the concept of using a Li_2MnO_3 component to stabilize layered LiMO_2 structures with the ultimate objective of stabilizing layered LiMnO_2 . In particular, we expanded our synthesis efforts to include solid solutions of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ compositions, where M = Mn, Ni or Co, or a combination thereof. Optimized compositions have yielded specific capacities of ~ 150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C , but for less than 100 cycles.

EXPECTED STATUS SEPT. 30, 2001: Improvements in the electrochemical performance of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been achieved. A performance target of 150 mAh/g for 100 cycles at 50°C in Li/ $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ cells has been set. A more detailed understanding of the behavior of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been gathered. Work on stabilized $\alpha\text{-MnO}_2$ electrodes for Li-polymer cells will have been initiated in collaboration with LBNL (J. Kerr) with an initial target reversible capacity set at 200 mAh/g for 50 cycles.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: The initial milestone (#1) to be reached by the end of April 2001 will be to achieve a reversible electrochemical capacity of 150 mAh/g from layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes for 50 cycles at 50°C against a metallic Li counter electrode. This will be increased to 100 cycles by the end of September 2001 (#2). By then a more detailed understanding of the electrochemical and structural relationships of layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will also have been gathered.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone 1 over last quarter**

Over the past quarter, the synthesis of various compositions of $[x(\text{Li}_2\text{MnO}_3) \bullet y(\text{LiMO}_2)]$ phases was continued, with an emphasis on $M=\text{Mn}$ or Ni . Some materials have been phase pure while others were not. In particular, the formation of pure Mn-based systems appears to be compromised by the thermodynamic stability of orthorhombic LiMnO_2 that tends to form when trivalent Mn is reacted with Li salts. To circumvent this, we have attempted high-temperature quench experiments to promote the formation of $[0.33(\text{Li}_2\text{MnO}_3) \bullet 0.66(\text{LiMnO}_2)]$, but we have had limited success.

One Ni-based composition that showed promising results was $[0.1(\text{Li}_2\text{MnO}_3) \bullet 0.9(\text{LiNiO}_2)]$. This material was fabricated into an electrode laminate and cycled in a Li coin cell. The electrochemical data are shown in Fig. 1. The voltage profile contains three plateaus that do not change appreciably over time, unlike cells with pure LiNiO_2 electrodes. We attribute this to stacking faults that are introduced by micro-crystalline Li_2MnO_3 domains that are distributed throughout the composite structure. TEM experiments and post-test x-ray diffraction analyses are underway in attempts to validate our interpretation.

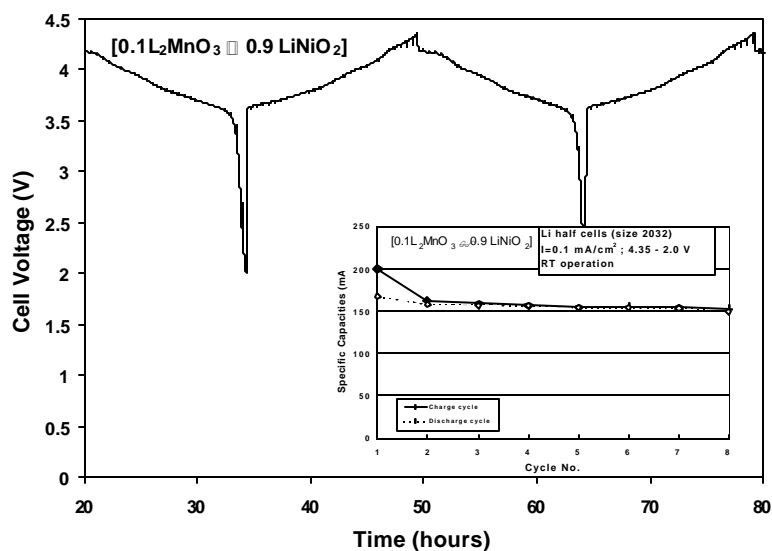


Figure. 1. Voltage profile of a Li coin cell containing a composite cathode $[0.1(\text{Li}_2\text{MnO}_3) \bullet 0.9(\text{LiNiO}_2)]$. The inset shows a plot of specific capacity vs. cycle number. The electrode provides a steady 150 mAh/g for the first 10 cycles.

- Further plans to meet or exceed milestones:** None
- Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/Polymer/Gel and Low-Cost Li-Ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2000: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can also be stabilized by the addition of manganese ions

EXPECTED STATUS SEPT. 30, 2001: For low-cost Li-Ion cells, we expect to identify the changes in LiMnO_2 structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized LiMnO_2 and to increase its electrochemical capacity, to understand better the behavior of the $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$ cathode and to determine if there is an iron analog. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized δ -vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are:

- 1 to characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg.
- 2 complete the characterization of manganese-stabilized vanadium oxides and to compare the best samples with iron phosphates for polymer or gel batteries by July 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter**

Earlier we formed a vanadium-oxide pillared manganese oxide [*Electrochem. Commun.* **2**, 445, 2000]. We have cycled this material at both 0.1 mA/cm² and 1 mA/cm² and see no evidence for the formation of the spinel-like two-step electrochemical discharge/charge curves. This is in direct contrast to either Li_xMnO₂ or the pillared K_xMnO₂ which both show conversion to a spinel-like phase on the first charge/discharge cycle. The capacity of the vanadium-oxide pillared manganese oxide is 150 Ah/kg but drops below 100 Ah/kg on increasing the discharge rate to 1 mA/cm². We will be seeking to increase the capacity.

- **Further plans to meet or exceed milestones:** None

- **Reason for changes from original milestones:** N/A

- **Accomplishments toward milestone 2 over last quarter**

Our original manganese-stabilized δ -V₂O₅ compound was a mixture of two phases. It has a very respectable 220 Ah/kg discharge capacity [*Electrochem. Commun.* **2**, 69, 2000]. In an attempt to identify the electrochemically active phase(s) we have succeeded in preparing a pure phase of one of the two components. This material, [(CH₃)₄N]_{0.2}Mn_yV₂O₅, has a lattice repeat distance of 13Å, and contains only 0.06 Mn per V₂O₅; it is thermally stable to above 250°C with no structural changes. Its initial capacity is 220 Ah/kg with a mean discharge potential of 3 V and very little polarization. However, increasing the manganese content from 0.06 to 0.1 drops the capacity to 180 Ah/kg as shown in Fig. 1.

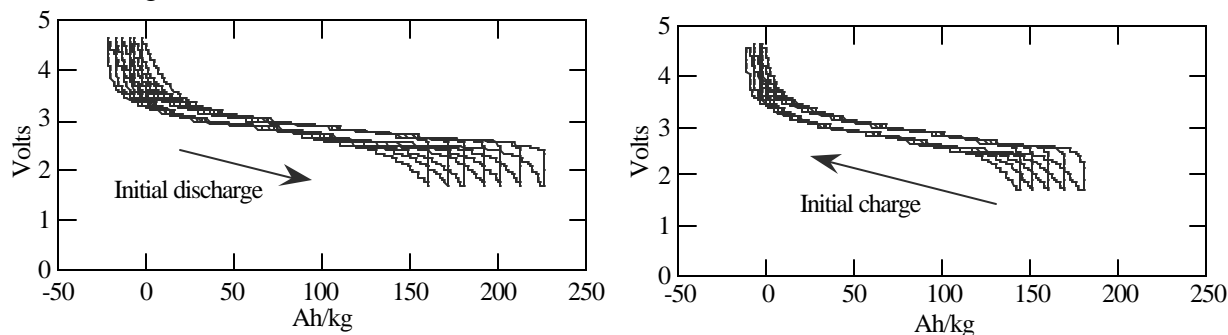


Figure 1. Capacity of manganese stabilized vanadium oxides, (left) Mn=0.06, and (right) Mn=0.10

- **Further plans to meet or exceed milestones:** None

- **Reason for changes from original milestones:** N/A

Presentations

Invited presentations were made at the Japanese National Battery Meeting, Nagoya, Japan – November 2000, Int. Symposium on Solvothermal Synthesis, Tokyo, Japan – December 12, 2000.

Seminar on “Lithium Batteries” at NTT Laboratories, Ibaraki, Japan, December 14, 2000.

K. Ngala, P. Y. Zavalij and M. S. Whittingham, “Manganese vanadium oxide compounds as cathodes for lithium batteries,” presented at Electrochemical Society Meeting, Phoenix, AZ, October 2000; Materials Research Society in Boston, MA, December 2000.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes -Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The micro-structures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2000: A tunnel-containing manganese oxide has been cycled more than 700 times in a Li/liquid electrolyte cell configuration, with little capacity loss and no structural change. Cells can be discharged repeatedly at up to 5 C rate with no damage. The effect of Ti-substitution upon the electrochemical characteristics has been determined, and a correlation between unit cell size and capacity has been observed.

EXPECTED STATUS SEPT. 30, 2001: The program will be expanded to include lithium iron phosphates and substituted spinels as required by the BATT program. We expect to have prepared samples of LiFePO_4 available for the program and to have made a preliminary determination of the electrochemical characteristics. We also will have determined if anion substitution of tunnel-containing manganese oxides is a viable approach to improving capacity.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: Our major milestone this year is to provide small samples (30 g) of conventional LiFePO_4 to the BATT program by early 2001. We are on schedule.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Materials for the synthesis of LiFePO_4 were purchased, and preparation is expected to start shortly. Cycling of $\text{Li/P(EO)}_8\text{LiTFSI/Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ cells was completed during this quarter. The figure shows results for three cells discharged under different conditions.

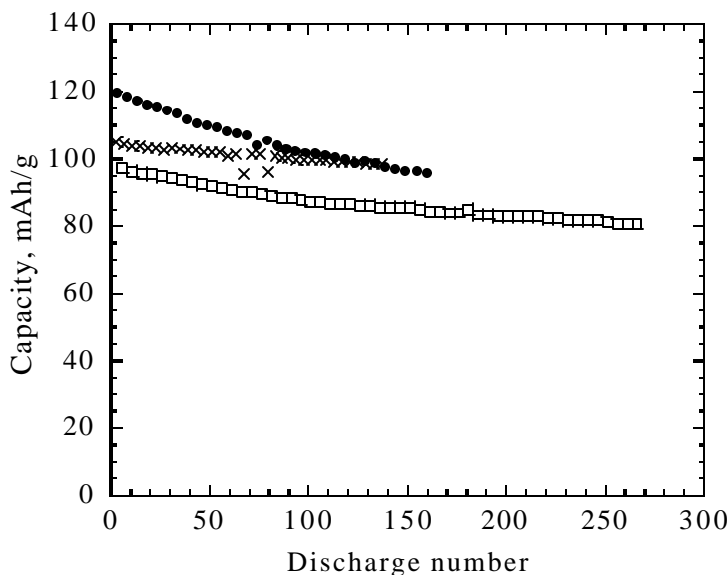


Figure 1. Capacity as a function of cycle number for $\text{Li/P(EO)}_8\text{LiTFSI/Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ cells discharged at 0.1 mA/cm^2 between 3.6 and 2.4V (●), 0.1 mA/cm^2 between 3.6 and 2.5 V (×), and 0.5 mA/cm^2 between 3.6 and 2.5V (□).

The highest initial capacity is found for the cell discharged at 0.1 mA/cm^2 between 3.6 and 2.4V. Fading is markedly faster than for the cell discharged at the same rate between 3.6 and 2.5 V (an average loss of 0.17% compared to 0.04%), so the advantage is lost once the cells are cycled more than 140 times. A cell discharged at a higher current density (0.5 mA/cm^2) between 3.6 and 2.5 V showed a lower initial capacity and lost an average of 0.06% per cycle. While the initial capacity is somewhat improved over that of Li_xMnO_2 at low to moderate rates, the advantage is lost once the current density is increased, and the cycling behavior, although good, is not as impressive (Li_xMnO_2 loses less than 0.02% of its capacity per cycle, on average, when discharged at 0.5 mA/cm^2). The reasons for this have been covered in the last quarterly report. For this reason, we have decided to investigate substituents other than Ti in our quest to increase the capacity of tunnel-containing MnO_2 s without compromising the excellent cycling and rate behavior.

Presentation

“Novel Tunnel-containing Manganese Oxides with Excellent Reversibility” presented by M. Doeff at the DOE Workshop on Interfaces, Phenomena, and Nanostructures in Lithium Batteries, Argonne, IL, December 11-13, 2000.

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

ETR TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Data to be collected include changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2000: We defined the relationships between electrode history, electrolyte composition, electrode surface properties, and temperature for a model thin-film spinel LiMn_2O_4 cathode.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify changes in $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode surface morphology and chemistry which accompany cycling in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and identify or confirm specific degradation modes. We expect to characterize SEI formation and growth on lithium and carbonaceous anodes in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and determine the role of SEI growth in cell capacity and power loss.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to determine the effect of sulfur additives on the surface chemistry of LiMn_2O_4 electrodes is expected to be completed by the planned date of April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have characterized in detail the surface phase segregation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes taken from ATD Gen 1 Li-ion cells. This work serves three purposes: (i) to enhance the capabilities of our diagnostic techniques for the study of BATT Program electrodes, *e.g.*, identifying the role of sulfur additives on electrode surface chemistry; (ii) to provide better understanding of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ interfacial processes; and (iii) to support ATD Program diagnostics. Our original discovery of changes in cathode morphology and surface composition was made during routine diagnostic tests of ATD Program cells, however much more work is needed to identify the root cause(s) of these changes and identify methods to avoid them.

A “reference library” was constructed by recording Raman spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders and commercially available materials, and collecting literature data. Raman microscopy was used to determine the micron-scale structural integrity of these materials and compare their spectral characteristics with those of LiNiO_2 and LiCoO_2 . LiNiO_2 and LiCoO_2 exhibit pairs of well-defined vibration bands at 468, 546 and 487, 597 cm^{-1} , respectively. In contrast, micro-Raman spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders exhibit one broad maximum centered at $\sim 520 \text{ cm}^{-1}$ and a sharp peak at $\sim 555 \text{ cm}^{-1}$. Such spectral characteristics are typical for a solid solution of Co-substituted nickel oxides, rather than a mixture of new crystalline phases. We observed slight variations in the shape of the broad band at 520 cm^{-1} for different samples, and to a lesser extent among different grains in the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder. These inhomogeneities stem from slight variations of surface composition and structure of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ grains.

Micro-Raman spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes taken from Gen 1 cells stored or cycled at elevated temperatures ($\geq 40^\circ\text{C}$) display significant spectral changes. The originally featureless broad maximum at 520 cm^{-1} split into separate bands at 479, 553, and 565 cm^{-1} , and a weak shoulder at $\sim 600 \text{ cm}^{-1}$ because of a thermally induced surface phase segregation process. Exposure of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ to LiPF_6 -EC-DEC at room temperature revealed no significant electrode surface changes.

Neither substitution of Ni with Co nor Li intercalation-deintercalation changes the $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ R3m space group symmetry. However, Co substitution of Ni(III) oxides increases the crystal lattice parameter, as reflected by a $3\text{-}4 \text{ cm}^{-1}$ shift of two characteristic $474/554 \text{ cm}^{-1}$ NiO_2 bands toward lower frequencies and an increased $474/554$ peak ratio. Lithium intercalation into NiO_2 has the opposite effect: the bands shift toward higher frequencies and the $474/554$ peak ratio decreases. The presence of separate bands at both sides of the original NiO_2 peaks and strong relative peak intensity variations in the spectra of Gen 1 cathodes suggest the formation of stable crystalline phases of Ni(III) or Ni(IV) oxides with different amounts of Co and Li on the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode surface.

- **Further plans to meet or exceed milestones**

We are preparing a series of thin-film LiMn_2O_4 electrodes and will study the effect sulfur on their electrochemical performance.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Structure and Characterization of Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge x-ray absorption spectroscopy and transmission electron microscopy (TEM).

STATUS OCT. 1, 2000: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel LiMn_2O_4 cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of LiMn_2O_4 cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify the changes in $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ when cycled in LiPF_6 -EC-DMC electrolyte. We also expect to develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Completion of XAS studies of LiCrMnO_2 by April 2001.
2. Completion of XRD and XAS studies of $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_4$ by June 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter**

The experimental work on XAS of LiCrMnO_2 has been completed. The data are complex and are being analyzed. A paper will be prepared for publication.

- **Further plans to meet or exceed milestones**

None

- **Reason for changes from original milestones**

N/A

- **Accomplishments toward milestone 2 over last quarter**

Three $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ materials ($x = 0.1, 0.3$ and 0.5) were prepared by a sol-gel process. All are single-phase spinel materials. XRD was completed on $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$. The data are undergoing Rietveld analysis. XAS has been completed on both $\text{LiNi}_{0.3}\text{Mn}_{1.7}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

- **Further plans to meet or exceed milestones**

None

- **Reason for changes from original milestones**

N/A

LBL TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2000: We identified one of the mechanisms of SEI layer formation on carbon anode in EC-based electrolytes.

EXPECTED STATUS SEPT. 30, 2001: Establish thermal stability of the SEI layer on graphite anodes in GEN 2 electrolyte. Identify some routes to improved stability *via* electrolyte additives and/or graphite pre-treatment.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to install and calibrate a new IR microscope is postponed to April 2001 due to the delay of equipment funds. Another new milestone is set to demonstrate that one of our diagnostic techniques can identify a failure mechanism in a Li-ion battery.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** A purchase order for IR microscope was placed. It was demonstrated that AFM is useful in detecting SEI layer formation, a step towards identifying SEI layer formation mechanism.
- **Further plans to meet or exceed milestone:** XPS and AFM will complement the FTIR results in identifying a failure mechanism in Li-ion battery.
- **Reason for changes from original milestone:** This milestone was postponed to April 2001 due to the delay of equipment funds.
- **Accomplishments toward milestone 2 during last quarter:** The role of vinylene carbonate (VC) as additive in Li^+ ion electrolyte was further investigated by *in situ* Atomic Force Microscopy (AFM). A solution with 1 vol% of VC in THF with 0.1 M LiClO_4 was used as the electrolyte. A polished glassy carbon (1.2 x 1.2 cm) was employed as the working electrode with Li metal as both the reference and counter electrode. The potential was stepped down from 2 to 0.5 V with 100 mV interval. Surface profiles were scanned at each step. The data indicate that a surface film was starting to develop on the electrode surface at 1.2 V. The AFM images at open circuit potential and 1.2 V are shown respectively in Figs. 1A and 1B below. This finding is consistent with the reduction of VC in THF reported previously by our group (Fig. 2). The thickness of the surface film was measured to be ~10 nm. This observation confirms our previous conclusion that VC is forming a SEI layer at high potential before Li^+ intercalation into graphite and therefore prevents solvent co-intercalation.

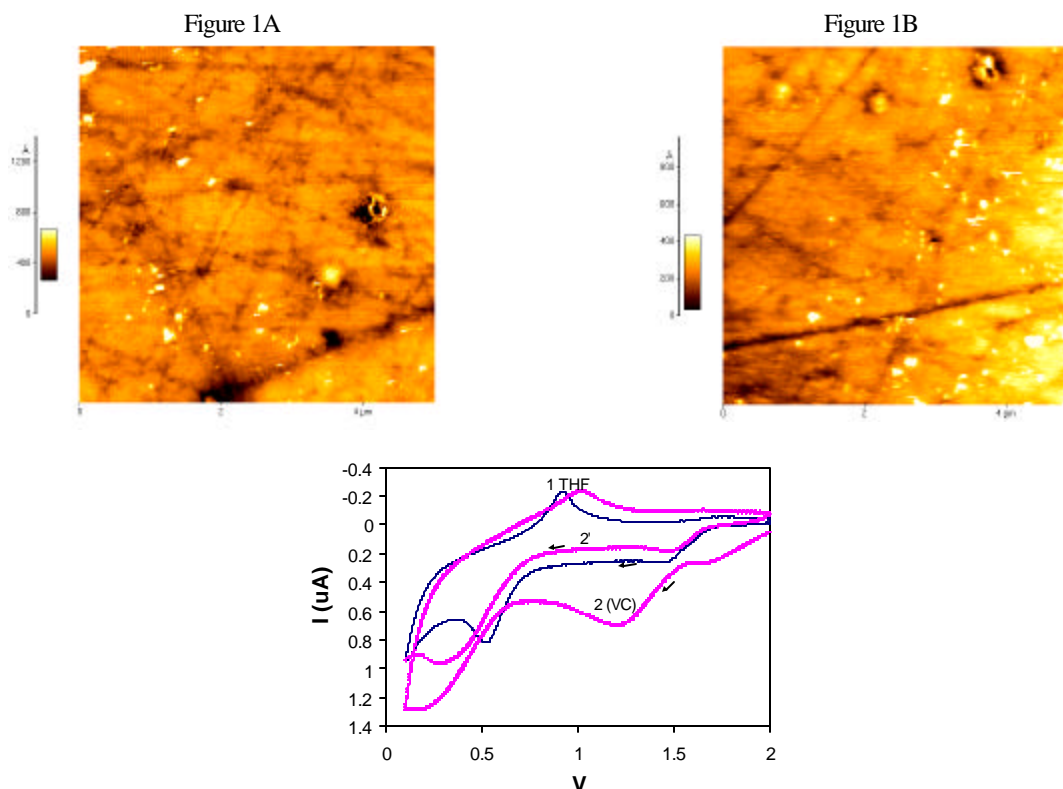


Figure 2. Cyclic voltammetry for THF-based electrolyte (1) without target solvent species, and (2) with VC dissolved within (2 for the 1st cycle and 2' for the 2nd cycle). Only reduction on the 2nd cycle is shown.

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: E. J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-Ion and Li-polymer Batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling; and (2) to synthesize intermetallics that have higher capacities than carbon electrodes and that demonstrate stable capacities during cycling.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. We prepare intermetallics in the Mg-Sn system by mechanical alloying. Characterizations are performed with x-ray diffraction and microscopy techniques.

STATUS, OCT. 1, 2000: Milling conditions to synthesize cubic and rhombohedral forms of Mg_2Sn were determined. Amorphous Mg-Sn alloys could not be produced by mechanical alloying in a typical high-power ball-mill. Attempts to synthesize a metastable, cubic $\text{Mg}_{5.67}\text{Sn}$ alloy were started. Cycling tests showed that cubic- Mg_2Sn capacities can exceed capacities for carbon electrodes, but the capacities fade below 100 mAh/g after a few cycles. Comparisons between fine-grained Mg_2Sn and coarse-grained Mg_2Sn show that the microstructure of these intermetallics influences electrochemical performance. X-ray diffraction of cycled electrodes indicates that a major mechanism for the capacity decay is conversion of the intermetallic into Mg and Sn.

EXPECTED STATUS SEPT. 31, 2001: We expect to have concluded our evaluation of the Mg-Sn system. We plan to perform nuclear magnetic resonance experiments to aid in the characterization of the microstructure of the intermetallics and to determine sites that are occupied by Li. We expect to have identified the role of the microstructure in Mg_2Sn , studied through experiments on as-milled samples and on annealed samples, on the electrode capacity and cycle life. Similar work will be performed on the metastable, rhombohedral- Mg_2Sn phase to determine if this more conductive phase retains its structure during cycling.

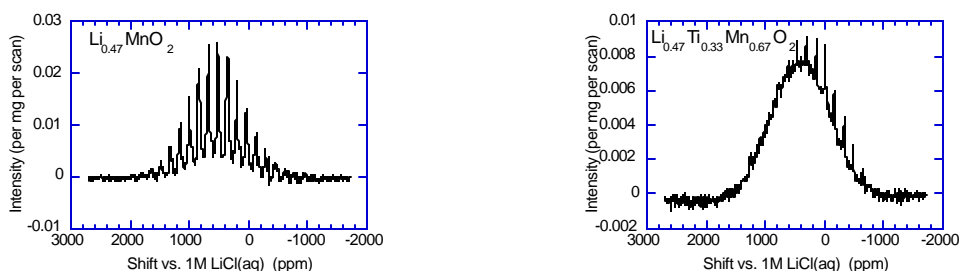
RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to compare NMR-observable properties of stoichiometric and substituted tunnel-structure electrodes before and after cycling, and to complete work on the cubic- Mg_2Sn phase by April 2001.

PROGRESS TOWARDS MILESTONES

- Accomplishments toward milestone during last quarter**

Preliminary ^7Li MAS NMR spectra have been acquired for several tunnel-structure materials. These spectra were obtained using a 181 MHz magnet, and thus show substantial linebroadening arising from coupling between the Li nucleus and unpaired manganese d-electrons. Representative spectra are shown below.



These spectra indicate the existence of several chemically distinct types of lithium. In fact, the Ti-substituted composition shows significant spectral overlap arising from a wide variety of lithium sites.

Appropriate milling conditions and heat treatments to produce a crystalline cubic Mg_2Sn phase, a nanocrystalline cubic Mg_2Sn , and a rhombohedral Mg_2Sn phase were determined. XRD and TEM showed that the as-milled materials had poorly shaped grains that did not significantly grow after nucleation. Differences in the electrochemical performance between the as-milled materials and the highly crystalline, annealed materials were noticeable. XRD results for cycled electrodes showed that significant conversion of the intermetallic into Mg and Sn occurs during cycling.

- Further plans to meet or exceed milestone**

Future work will use a 100 MHz magnet. Greater resolution is expected, and isotropic peaks will be assigned by comparison of spectra obtained at both fields. It is expected that resolution will be improved to the point that relaxation times and linewidths will be obtainable for each isotropic peak. Knowledge of relaxation times will allow the determination of a quantitative relationship between lithium content and Li NMR signal intensity.

We will attempt to use Sn NMR to quantitatively determine the amount of Sn in different environments in the Mg_2Sn intermetallics, particularly the amount of Sn in defect sites. This may help explain the differences in electrochemical performance between the samples with different microstructures. Cycling will be performed with higher voltage cutoff limits to try to reduce the conversion of Mg_2Sn into Mg and Sn during electrode charging.

- Reason for changes from original milestone: N/A**

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - EQCM Studies of the SEI on Carbon Anodes

SYSTEMS: High-power Li-ion battery

BARRIER: Irreversible capacity loss due to SEI formation and growth

OBJECTIVES: The primary objective is to understand SEI formation and growth on carbon anodes.

APPROACH: Our approach is to use an electrochemical quartz crystal microbalance (EQCM) to characterize the SEI formed on disordered carbon thin-film electrodes in model cells. Data to be collected are changes in mass of the SEI on the electrode and, thereby, the SEI growth with cell cycling is studied. A joint study to combine spectroscopic ellipsometry and EQCM gives us the SEI density.

STATUS OCT. 1, 2000: We estimated the SEI density on disordered carbon thin-film electrodes and observed mass changes corresponding to Li intercalation/deintercalation in 1M LiClO₄ / EC+DMC electrolyte.

EXPECTED STATUS SEPT. 30, 2001: We expect to correlate SEI formation and growth with the electrolyte LiPF₆ or LiTFSI / EC+DMC electrolyte and impurities (*e.g.*, H₂O).

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Our major milestone to study the dynamic nature of the SEI as a function of electrolyte composition during cycling is expected to be completed by the planned date of July 2001.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone over last quarter**

A model was developed for interpretation of past data obtained in EQCM and cyclic voltammetry experiments. The model shows that while the total charge measured during cyclic voltammetry is due to SEI growth ($Q_{n,SEI}$) and Li intercalation ($Q_{n,Li}$), the total frequency change results from chemical reactions ($-\Delta f_{n,t}$) as well as Li intercalation ($-\Delta f_{n,Li}$) and electrochemical reactions in SEI growth ($-\Delta f_{n,SEI}$). The following are the equations that outline the model.

$$Q_n = Q_{n,SEI} + Q_{n,Li}$$

$$(-\Delta f_n) = (-\Delta f_{n,SEI}) + (-\Delta f_{n,Li}) + (-\Delta f_t)$$

Figure 1 contains the frequency change plotted vs. time during cyclic voltammetry and some frequency changes calculated based on the model. The chemical reaction term is estimated using the frequency change at OCV in the last quarterly. By eliminating the contribution of Li intercalation and chemical reactions from the measured frequency change, the frequency change due to SEI can be separated, and this term is expressed as:

$$-\Delta f_{SEI} = \frac{C_f}{F} (mpe_{n,SEI} - mpe_{Li}) Q_{n,SEI}$$

where C_f and F are constants, and $mpe_{n,SEI}$ is the mass per electron of SEI formed at the n th cycle. The blue curve ($-\Delta f_{SEI}$) approaches zero with time and this means that the charge for the SEI decreases with cycling. After the 16th cycle (about 60000 sec) under our experimental conditions, the SEI ceases to grow.

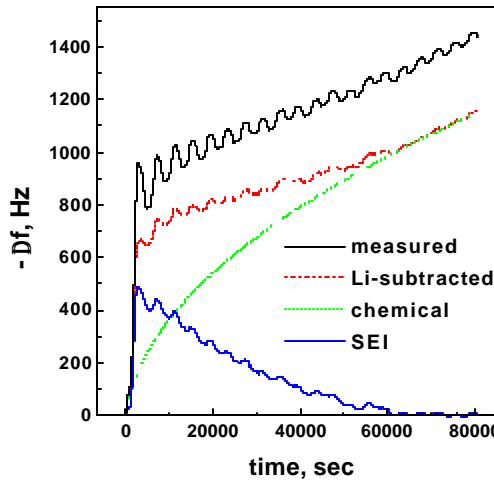


Figure 1. Frequency change plotted vs. time during cyclic voltammetry (20 cycles at 1mV/s in $\text{LiClO}_4 / \text{EC} + \text{DMC}$) and some frequency changes calculated for the analysis.

- Further plans to meet or exceed milestone**

Cyclic voltammetry, with experimental conditions the same as before, will be conducted for $\text{LiPF}_6/\text{EC} + \text{DMC}$ or $\text{LiTFSI}/\text{EC} + \text{DMC}$ electrolytes. The same analysis for SEI formation and growth will be made and the results will be compared with our past results on $\text{LiClO}_4/\text{EC} + \text{DMC}$.

- Reason for changes from original milestone:** N/A

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Poor polymer transport properties, thermal management, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use potentiometric technique to measure entropy and develop thermal model that accounts for concentration effects in insertion electrodes, in order to improve thermal management. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2000: Measured transport properties in PEO-LiTFSI polymer electrolyte and improved the measurement technique. Completed computer program and simulations for electrolyte diffusion coefficient of NaCl and KCl in water. Used calorimetry to validate energy balance. Measured entropy in manganese oxides. Developed a preliminary model for dendrite growth which includes effects of surface tension. Developing Raman spectroscopy methods to examine dendrite growth *in situ*.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete measurements of the transport properties of PEO-LiTFSI and to complete refinement of both the galvanostatic polarization method and the transition-time verification method. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes currently of interest to the BATT program, such as LiBF₄ in EC:PC, will be ongoing. Measurements of the entropy of reaction in BATT baseline materials will be completed. Modeling of the SEI layer will be ongoing. Refinement of a model of dendrite growth to include relevant physical effects will be ongoing, as will experimental work to observe dendrite growth and concentration profiles *in situ* using confocal Raman spectroscopy.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES: Milestone 1 to model agglomeration in tin composite oxide (TCO) has been changed to developing a preliminary model of transport through the SEI layer by August 1, 2001. Milestone 2 to design a cell container for *in situ* confocal Raman microscopy is added for July 1, 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:**

With Steve Sloop and John Kerr, we completed measurement of the transference number and diffusion coefficient on the PEMO-LiTFSI system at 85°C. Results were presented at the Oct. 2000 meeting in Phoenix and in a subsequent proceedings paper. Unlike previous reports, negative values of the transference number were calculated at low concentrations, possibly due to side reactions and/or ion association. Transition-time experiments were also made as part of this study and were consistent with the occurrence of side reactions.

Changes to the molecular dynamics computer code to permit simulation of carbonate solvent molecules are ongoing. In addition, we are attempting to ascertain the simulation-size dependence of the diffusional properties, so that we may optimize the simulation size. Difficulties with the simulation algorithm have been encountered due to the planar structure of many of the carbonates.

We have conducted a literature review to determine which design options appear to successfully address the issue of loss of contact in alloy electrodes. We have learned that there are three simultaneous factors contributing to loss of contact: alloy expansion and contraction leading to cracking and particle contraction away from a continuous electrical path to the current collector, SEI formation around freshly exposed surface area, and particle agglomeration causing increased stresses during lithiation and delithiation. Therefore any design option must 1) either involve no volume change or create a driving force to push particles together during contraction, 2) prevent resistive compounds from forming between particles during volume change, and 3) prevent particle agglomeration. Although TCO slows particle agglomeration to some extent, it does not create a driving force to push particles together during contraction since the composite oxide is rigid and brittle and does not participate in any reformation reaction.

The entropy of reaction as a function of state of charge was measured in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and in graphite MCMB 25-28. Measurements for tunnel LiMnO_2 and other baseline materials in the BATT program are planned for next quarter.

- **Further plans to meet or exceed milestone:** The focus of this modeling project will shift to modeling the effects of the SEI layer on interparticle contact.
- **Reason for changes from original milestone:** Result of literature review.

- **Accomplishments toward milestone 2 during last quarter**

The model of dendrite growth completed in September, which accounts for kinetic, concentration, and surface-energy effects on potential, has been modified to allow the gathering of more data in the simulation. A preliminary analysis using elasticity theory has shown that the mechanical properties of the separator affect dendrite growth more significantly than surface forces; furthermore, the plasticity of the Li surface needs to be accounted for in the mechanical analysis. The construction of parallel electrode cells for *in situ* observation of dendrite growth and concentration profiles in polymer electrolytes has undergone several design revisions. Further modifications are needed to build a cell configuration that is airtight, inert, transparent, and fits inside the confocal Raman microscope.

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A (new milestone)

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2000: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2001: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by Argonne National Laboratories, by May 31, 2001 (start date: 2/01).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have continued simulations development, culminating in a general-purpose solver for determination of conductivity of irregularly-spaced and shaped particles. These particles are representative of carbons in the anodes of the Li-ion cells that we intend to study. We have also made progress in mechanics simulations of stresses at particle junctures. Our main accomplishments thus far are:

1. conductivity code for automatic generation of irregular arrays of conductive particles, and code benchmarking against classical models
2. mechanics modeling of interconnects, accounting for "fillet" intersections in 3D synapses, and detailed comparison with previous 2D modeling

- **Further plans to meet or exceed milestones**

We have an agreement with ANL to supply cycled and uncycled batteries/components, particularly Li-ion anodes of type Gen 1 and Gen 2, for study. We also have, ahead of schedule, begun development of a conversion of 2D simulations to allow incorporation of 3D results, in mechanical simulations of interfacial stresses.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Thermal Modeling of Li Batteries

SYSTEMS: Li-polymer (Li-ion)

BARRIER: Thermal management and safety issues, battery efficiency.

OBJECTIVES: The objective is the ability to predict the thermal behavior (including stability) and efficiency of Li batteries for use in electric or hybrid vehicles.

APPROACH: The approach is a combination of mathematical modeling and experimental measurement. The modeling couples the numerical solution of the equations for heat generation and transport within a battery to the equations describing battery electrochemistry.

The experiments are to measure fundamental properties for input into the model or for comparison with model predictions. Thermal conductivities of cell components are measured, as are heat generation rates, in laboratory and commercial cells.

STATUS OCT. 1, 2000: A coupled mathematical model had been developed and found to show a reasonable fit to limited experimental data on heat generation during discharge of laboratory Li-polymer cells.

EXPECTED STATUS SEPT. 30, 2001: Refinements of the mathematical model will be completed. The electrochemical calorimeter will be used to measure the heat generation rate of a limited number of commercial Li-ion batteries.

RELEVANT USABC GOALS: 75-80% discharge efficiency, thermal loss 15% of capacity in 48hrs, safety.

RELEVANT USABC GOALS: Tolerance to abusive operating conditions.

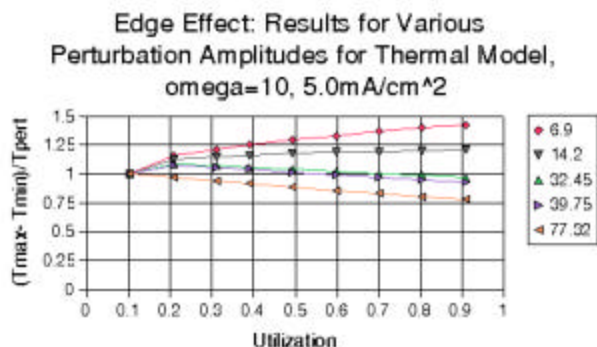
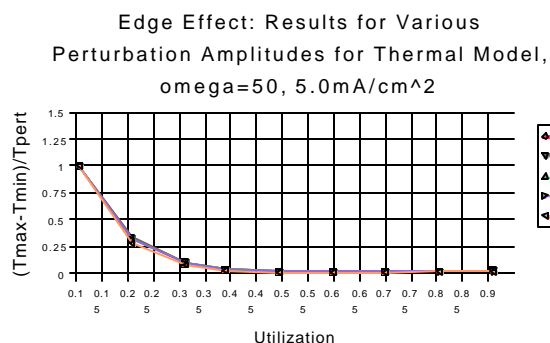
MILESTONES: Completion of measurements on Li-polymer cells available under the BATT program - September 2001

PROGRESS TOWARDS MILESTONES

Accomplishments towards milestones over last quarter

Previous work at LBNL has shown that the Li/polymer cell is inherently unstable with respect to perturbations of large length scales under conditions representative of planned application. That is, any overheated region becomes a site for enhanced heat generation, and thereby for further escalation of the temperature. Fortunately, it appears that the rate of escalation is sufficiently low that this instability will present a danger only with repeated cycles at high charge/discharge rates. This instability is more significant for perturbations with a large length scale because ones of small length scale can be dissipated by conduction. Accordingly a closer examination of large length scale perturbations, particularly ones with a length scale comparable to the dimensions of the cell stack has been carried out.

Perturbation analysis presented in previous work, Song (1997), suggests that in batteries with dimensions of about 0.5 meters, thermal perturbations should grow when the wavenumber of the perturbation falls below 15. Upon closer examination, one finds that when the wavenumber reaches 15, the wavelength of the perturbation is nearly the dimension of the battery; therefore the tenets of perturbation theory are questionable. This can be demonstrated by examining the results of a 2D simulation for perturbations with varying wavenumber and amplitudes, as shown in the figures below. The plots show the development of the trough-to-peak temperature difference of a sinusoidal perturbation, normalized by the initial value of that difference. Omega is the wavenumber (m^{-1}) and the stack is discharging at $5 \text{ mA} \cdot \text{cm}^{-2}$. When the wave number is large, and the wavelength of the perturbation is much smaller than the dimension of the battery, the results from the simulation are independent of the amplitude of the perturbation (K). Furthermore the stack is stable i.e. the wave is decaying as discharge proceeds. However, when the wavenumber is small, the results are dependent on the amplitude and therefore the results from the perturbation analysis, including whether the perturbation grows or diminishes, become dependent on the amplitude and position of the perturbation.



Further plans to meet or exceed milestones:

The electrochemical calorimeter that is to be used for measurement of heat generation in Li-polymer cells is currently not operating. We are working with the manufacturer to determine the difficulty and anticipate a functioning and working calorimeter by April. The calorimeter will then be used for heat generation measurements on cells becoming available (*e.g.*, from HydroQuébec) at that time.

Reasons for changes from original milestones: N/A

PROPOSALS UNDER REVIEW

ORGANIZATION <i>(Principal Investigator)</i>	TITLE	STATUS
Illinois Institute of Technology <i>(J. Prakash)</i>	Development of Nonflammable Electrolytes for Lithium-Ion Batteries	Renewal Proposal - Under Review
Northwestern University <i>(K.M. Abraham)</i>	Highly Conductive Polyelectrolyte-Containing Rigid Polymers for Lithium or Lithium-Ion Batteries	Renewal Proposal - Under Review
Covalent Associates <i>(A.B. McEwen)</i>	Non-Flammable Electrolytes for Lithium-Ion Batteries	Renewal Proposal -
North Carolina State Univ. <i>(Khan, Fedkiw, Baker)</i>	Composite Polymer Electrolytes for Use In Lithium and Lithium-Ion Batteries	Renewal Proposal - Under Review
HydroQuébec <i>(K. Zaghib)</i>	Research on Lithium-Ion Polymer Batteries Utilizing Low Cost Materials	Unsolicited Proposal - Under Review
University of Michigan <i>(A.M. Sastry)</i>	Failure Mechanisms in Li-Ion Systems: Design of Materials for High Conductivity and Resistance to Delamination	Renewal Proposal - Under Review

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT FOR OCTOBER – DECEMBER 2000

CALENDAR OF UPCOMING EVENTS

October 2000

- 13 - 18 17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; electricevent17@aol.com).
- 22 - 27 198th Electrochemical Society Meeting - Phoenix, AZ (Brian E. Rounsavill, The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; www.electrochem.org) Hyatt Regency
- 23 - 28 7th Frumkin Symposium on Electrochemistry – Moscow, Russia (Prof. B.M. Grafov, Russian Academy of Sciences, A.N. Frumkin Institute of Electrochemistry, Leninsky prospect 31, 117071 Moscow, Russia; fax: 7-0959520846; vek@netra.elchem.ac.ru)

January 2001

- 4 - 7 3rd Hawaii Battery Conference (HBC2001) - Kamuela, HI (Dr. A.N. Dey, ARAD Enterprises, 39 Poko Place, Hilo, HI 96720; tel/fax: (508) 759-4617; lithium@capecod.net) The Outrigger Waikoloa Beach Resort
- 9 - 12 16th Annual Battery Conference on Applications and Advances - Long Beach, CA (Hitesh Somani, Conference Coordinator, Das, Annual Battery Conference, Dept. of Electrical Engineering, Cal State Long Beach, 1250 Bellflower Blvd., Long Beach CA 90840-8303; (562) 985-4605; fax: (562) 985-7561; battery@csulb.edu)

March 2001

- 11 - 14 14th IBA Battery Materials Symposium - South Africa (Edward Coombs, +27 13 7593500; fax: +27 13 7526002; ecoombes@deltaemd.co.za; Mike Thackeray, (630) 252-9184; fax: (630) 252-4174; thackeray@cmt.anl.gov) Kwa-Maritane Game Lodge
- 25 - 30 199th Electrochemical Society Meeting – Washington D.C. (Mr. Brian E. Rounsavill, The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; brian@electrochem.org; <http://www.electrochem.org/staff/brian/html>)

April 2001

- 2 - 5 Space Power Workshop – Redondo Beach, CA (Jackie Amazaki, 301-336-4073; Jacqueline.y.amazaki@aero.org; <http://www.aero.org/conferences/power>) Crowne Plaza
- 17 - 19 Batteries 2001 – Paris, France (www.batteries2001.com)

May 2001

- 11 - 14 PES 2001, Polymer Electrolytes Symposium – The Netherlands (Symposium Secretariat: c/o LGCE, P.O. Box 83005, NL-1080 AA, Amsterdam, The Netherlands; +31 20 679 3218; fax: +31 20 675 8236; PES2001@lgce.nl)

July 2001

- 1 - 6 International Conference on Materials for Advanced Technologies – ICMAT 2001 – Singapore (B.V.R. Chowdari, Department of Physics, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260; 65-874-2956; fax: 65-777-6126; phychowd@nus.edu.sg; <http://www/mrs.org.sg/icmat2001>)
- 9 - 13 International Conference on Electrified Interfaces: 9th in a Series on Non-Traditional Methods – Nova Scotia (Dr. Sharon G. Roscoe, Chemistry Dept., Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0; fax: 1 9025851114; sharon.roscoe@acadiau.ca)

September 2001

- 2 - 7 200 ECS - Joint International Meeting of ISE and ECS– San Francisco CA (Dr. O. Dossenbach; odossenbach@pingnet.ch)

May 2002

- 12 - 17 201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting (Brian E. Rounsavill, The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; brian@electrochem.org; <http://www.electrochem.org/staff/brian/html>)

June 2002

- 23 – 28 11th Interantioanl Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB 11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/011/imlb11.html>)

September 2002

- 3 - 8 53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut fur Physikalische Chemie II, Universitat Dusseldorf, Universitatsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49 2118112803; schultzj@rz.uni-duesseldorf.de)

October 2002

- 15 - 18 17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; electricevent17@aol.com).
- 6 - 11 202nd Electrochemical Society Meeting – Salt Lake City, UT (Brian E. Rounsavill, The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; brian@electrochem.org; <http://www.electrochem.org/staff/brian/html>)

August 2003

- 31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

September 2004

- 55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)